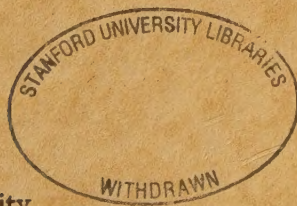


FACTORS AFFECTING THE STABILITY OF
ADDITION COMPOUNDS IN SOLUTION,
AND THEIR INFLUENCE UPON
IONIZATION EQUILIBRIA.

BY
PAUL M. GROSS, M. A., B. S.

DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE
OF COLUMBIA UNIVERSITY

New York City
1919



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**THE FACTORS AFFECTING THE STABILITY
OF ADDITION COMPOUNDS IN SOLUTION,
AND THEIR INFLUENCE UPON
IONIZATION EQUILIBRIA**

- (A) An attempt at a formulation and analysis of the factors upon which the ionic stability of solvent-solute complexes depends, together with the necessary experimental evidence in their support led to:
- (B) The essentially new measurements of the specific conductivities of fourteen binary systems, comprising acids with esters, ketones, bases and other acids.
- (C) As a result benefits to science in general will accrue from:
 - (1) The more definite formulation of a general ionic theory applicable to all concentration ranges and to non-aqueous as well as aqueous solutions.
 - (2) The initial steps in the development of a method for determining the existence and extent of compound formation in solution.

THE FACTORS AFFECTING THE STABILITY OF ADDITION COMPOUNDS IN SOLUTION, AND THEIR INFLUENCE UPON IONIZATION EQUILIBRIA

It is unfortunate that any attempt to modify the currently accepted ionization theory inevitably introduces a great many complicating factors, especially when solutions of finite concentration are considered. Compound formation between solvent and solute, changes in molecular complexity of solvent and solute, complex formation, etc.—all these are influences about which so little is definitely known that it becomes impossible to treat the question satisfactorily in a *strictly* quantitative manner. Before any real advances can be made towards a newer and more comprehensive theory it will be necessary to examine very closely the effect of these various factors upon the simple equilibrium between “ionized” and “non-ionized” solute.

Some initial steps in this direction have been attempted in preceding articles of this series.¹ The basis of the hypothesis there advanced is that ionization in solution is preceded by the formation of solvent-solute complexes, and that the disintegration of these into ions of opposite charge results from the diminished electrostatic attraction between the constituent radicals. The extent of ionization in any solution will consequently depend upon:

(a) The extent of compound formation—the degree to which reactions of the type $AB + CD \rightleftharpoons AB.CD$ proceed from left to right in a mixture of AB and CD in the liquid state; and

(b) The extent of the dissociation of these compounds into ions of opposite charge—the degree to which reactions of the type $AB.CD \rightleftharpoons (AB.C)^+ + D^-$ proceed from left to right in the mixture.

If the amount of compound formation is large and if these compounds are, ionically, extremely unstable, then the solution will exhibit a high conductivity. On the other hand, where there is little combination or where the compounds formed are comparatively stable ionically, the conductivity of the mixture can be but small.

We will, therefore, be able to *predict* the extent of ionization in any solution when we have once established what factors affect the formation and ionic stability of solvent-solute complexes in general. The first half of this problem has already been fully discussed² and it has been demonstrated experimentally that the extent of formation of addition compounds between solvent and solute (in other words the stability of complexes *with respect to their components*) increases uniformly with the differences in character (*i. e.*, in the positive or negative nature of the constituent groups) of these components. It is particularly note-

1. Kendall, Booge & Andrews, J. A. C. S., 39, 2302 (1917); Kendall & Booge, J. A. C. S., 39, 2326 (1917).

2. For résumé see Kendall, Booge & Andrews, J. A. C. S., 39, 2304 (1917).

worthy that complexes other than the simplest possible type AB.CD are formed in quantity only when AB and CD are decidedly diverse.

In the present paper the second half of the problem—the factors affecting the stability of solvent-solute complexes *with respect to their ionic dissociation products*—will be taken up. In their simplest form¹ the reactions here involved may be written: $AB.CD \rightleftharpoons (AB.C)^+ + D^-$. The case where AB and CD are identical molecules (or AB.CD is an associated pure liquid) may first be briefly considered.

The Ionization of Pure Liquids

Any liquid, the simplest molecules of which contain unsaturated atoms, will exhibit to a greater or less degree the phenomenon of association.² As a consequence of this association, the moments of the electrical doublets present in the simple molecules are considerably increased, and the constraints upon the electrons correspondingly diminished. The higher the degree of association, therefore, the less firmly are the constituent groups of the complex molecules held together, and the more readily will disintegration into ions of opposite charge take place. We should expect, then, that self ionization is in general a property *characteristic of highly associated liquids*.

In a series of liquids of similar type, arranged in order of ascending molecular complexity, a regular increase in specific conductivity should be apparent.³

Such is, in point of fact, the case. Ideal non-associated liquids (such as the saturated hydrocarbons) possess practically zero conductivity.⁴ Other *normal* organic substances (for example, benzene, chloroform, ether) are extremely poor conductors, the specific conductivity at 25° being of the order of 10^{-9} . When we examine the associated organic liquids,⁵ somewhat higher values are recorded in the literature: *e. g.*, formamide $S_{25} = 4.7 \times 10^{-5}$; acetone $S_{25} = 2.27 \times 10^{-7}$; formic acid $S_{25} = 6 \times 10^{-6}$; methyl alcohol $S_{25} = 1.45 \times 10^{-6}$.

Since the values for the specific conductivities of organic liquids in the literature are in general too high these will be discussed more critically later with the aid of the experimental data.

It is only when we come to consider fused salts⁶ where the molecular complexity may be as high as 8 to 10, that we find examples of pure substances highly dissociated into ions. The

1. The arguments which follow immediately below are independent of the actual formulæ of the complex or of its mode of ionization.

2. See Kendall & Booge, *J. A. C. S.*, 39, 2326 (1917).

3. The effect of other factors, some of which will be considered later, must, however, be borne in mind in the application of this rule. The viscosity of each liquid is a property to be taken into account in any comparison. See, particularly, Walden, *Z. Phys. Chem.*, 55, 246 (1906).

4. Scudder, *Conductivity and Ionization Constants of Organic Compounds* (1914).

5. Walden, *Z. physik. Chem.*, 46, 103 (1903).

6. Walden, *Z. Electrochem.*, 14, 723 (1908); *Londolt-Börnstein, Tabellen*, 1912, p. 1078.

following table¹ indicates clearly how specific conductivity varies with association in a typical series of chlorides. Unfortunately a strict comparison at one fixed temperature is impossible.

Substance	Association Factor ²	Specific Conductivity
NaCl	9 (810°)	3.34 (800°)
KCl	7 (778°)	2.19 (800°)
AgCl	2.25 (451°)	1.83 (500°)
PgCl ₂	2.05 (512°)	2.39 (520°)
SbCl ₃	1.55 (80°)	1.09 × 10 ⁻⁴ (80°)
POCl ₃	1.3 (0°)	2.2 × 10 ⁻⁶ (25°)
AsCl ₃	1.0 (25°)	1.24 × 10 ⁻⁶ (25°)
SO ₂ Cl ₂	1.02 (25°)	1.8 × 10 ⁻⁷ (25°)
CCl ₄ ; SiCl ₄ ; } SnCl ₄ ; SbCl ₅ ; } S ₂ Cl ₂ ; PCl ₃ }	1.00 (25°)	about 1 × 10 ⁻⁸ (25°)

Specific conductivity in a pure liquid, therefore, is primarily dependent upon the association factor. To go further we must ask the question: upon what does the degree of association of a pure liquid depend? Examination of the available data shows that here, just as in two component systems, the formation of complexes is conditioned by the differences in character (*i. e.*, in the positive or negative nature) of the several groups concerned. Thus in a substance like sodium chloride, where we have a highly electro-positive and a highly electro-negative con-

junction, ideal opportunity is afforded for the production of Na

highly associated molecules (either of the type NaCl
or NaCl NaCl), as has already been indicated.³ When differences in character are less pronounced, less association occurs (CCl₄, for example, is a non-associated liquid). We can, indeed, trace a general trend towards increasing or decreasing molecular complexity (so far as our elementary knowledge of association factors allows) as we proceed through any particular series of compounds, arranged in order of the electro-affinity of the variable radical. Thus hydrogen fluoride is highly associated even in the gaseous state and at ordinary temperature, hydrogen chloride is highly associated only when liquefied, while hydrogen bromide and iodide are only slightly associated even

1. Compare Turner, J. Chem. Soc., 99, 895 (1911).

2. The association factors given are the mean of those obtained by the surface tension method of Ramsay and Shields (J. Chem. Soc., 63, 1099 (1893), and by the specific cohesion equation of Walden (Z. physik. Chem. 65, 129 (1909)). Other methods of estimating association give here, in several instances, very divergent results (see Walden, Z. Electrochem., 14, 723 (1908)).

3. Kendall & Booge, J. A. C. S., 39, 2327 (1917).

as liquids at low temperatures.¹ In the same way, working along succeeding elements in the periodic system, we have:



and also:



Other illustrative examples will occur to the reader.²

Ionization in Solutions

From what has already been said it will be evident that a mixture of two ideal saturated substances (*e. g.*, two hydrocarbons) cannot give a conducting solution, also that the specific conductivity of a solution of an unsaturated substance in a saturated liquid (*e. g.*, hydrogen chloride in hydrocarbon) will be, in general, exceedingly small. In any case it will be *less* than that of the components when pure, since the degree of association of the solute (hence also its tendency towards ionization) will diminish with increasing concentration.

A mixture of *two* unsaturated substances, however, affords several possibilities. The results of actual experiment may be separated into three types. In the first, the specific conductivity of the mixture is not widely different from that of its components (usually very small); in the second, the conductivity is markedly greater, but still not exceptionally high; in the third, the conductivity is very great, even if the mixture is formed from two practically non-conducting substances.

The first case is typical of all mixtures in which the two components are similar in character (*i. e.*, for acids and bases, where the acidic or basic strengths are of the same order). Here there will be little or no increase in molecular complexity through compound formation on admixture—the chief effect rather will be mutual dissociation of any complex molecules of the pure components.³ Hence the conductivity of the solution will not differ greatly from that of its pure components, and

1. See Turner, J. Chem. Soc., 99, 890 (1911).

2. For full references on this topic see the monograph "Molecular Association," by Turner (Longmans, Green & Co., 1915).

3. An *apparent* exception is the case where *both* substances are highly associated (*e. g.*, in such a system as NaCl-KCl) when compounds of the general type $(\text{AB})_x(\text{CD})_y$ are undoubtedly formed in quantity. The *average* molecular complexity of the mixture, however (and hence its specific conductivity also), will not differ greatly from that of its pure components, since extensive dissociation of these is also involved. The complexes here existent are to be regarded, indeed, not as *addition* but as *substitution* compounds, for disintegration and recombination of the various ionic types present will evidently result, finally, in an almost "haphazard" replacement of the different radicals by one another at all points of the original molecules $(\text{AB})_x$ and $(\text{CD})_y$. A characteristic consequence of such indefinite combination is the production of "mixed crystals" on solidification, as for example in the chlorides of the alkali metals, Kurankov & Zemczuzny, Z. anorg. Chem., 52, 186 (1907).

(except in the case of mixtures of fused salts) will always be small. As samples, may be cited:

(a) Two very weak electrolytes—water and methyl alcohol.¹

(b) Two very strong electrolytes—trichloroacetic acid in hydrogen bromide.²

Numerous other instances may be found by reference to Scudder's "Conductivity and Ionization Constants of Organic Substances."

As the characters of the two substances begin to diverge, the extent of compound formation between them will become appreciable. Unless the divergence is very marked, however, the formation of complexes will be limited to the simplest type, and the degree of dissociation of this into its components in the liquid state will be very high. In other words, the addition of AB to CD involves the production of only a small amount of a molecular species AB.CD—the least complex (and consequently possessing the least tendency towards ionic disintegration) of all possible compounds. While, therefore, the conductivity of the solution may considerably exceed that of its components, it will still not be especially high. As examples may be given: any weak acid or base in water; hydrogen chloride in formic acid.³

If the two substances are decidedly diverse, extensive compound formation will occur on admixture. The complexes formed will include not only the simple type AB.CD, but also other and larger molecular species of the general formula (AB)_x.(CD)_y. Disintegration of these complexes into ions of opposite charge, taking place very readily, will render the solution an exceedingly good conductor. As examples may be given; any strong acid or base in water; methyl alcohol in hydrogen chloride.⁴

The essential features of a solution of high specific conductivity are, therefore: (a) unsaturation in both components; (b) a decided difference in the character of the two components. The first is necessary to enable compound formation to occur at all, the latter is the "driving force" which regulates the increase in molecular complexity (and hence in ionization) on admixture. The following additional examples will illustrate the uniform gradations experimentally observable as these factors are separately varied:

(a) *Unsaturation*. Hydrogen chloride in octane is a non-conductor, in benzene an exceedingly poor conductor, in ether a fair conductor, in alcohol a good conductor, in water an excellent conductor.

(b) *Diversity*. In liquefied hydrogen chloride⁵ as solvent, acetic acid is a good conductor, formic acid not so good, chlor-

1. Carrara, Gazz., 271, 422 (1897).

2. Walker, McIntosh & Archibald, J. Chem. Soc., 85, 1100 (1904).

3. Zanninovich-Tessarini, Z. physik. Chem., 19, 251 (1896).

4. Maass & McIntosh, J. A. C. S., 35, 540 (1913).

5. Walker, McIntosh & Archibald, loc. cit.

acetic and cyanoacetic acids poor conductors, trichloroacetic acid a non-conductor. The conductivity decreases regularly as the acidic strength of the solute approaches that of the solvent. Similarly Walden¹ considering the conductivity of solutions with water as solute finds that water in liquid HCN is a poor conductor, in formic acid a fair conductor, in sulphuric acid a good conductor.

The cases cited in the above discussion furnish evidence as to the probable validity of the hypothesis here advanced. They are, however, drawn from many sources of varying reliability and in some cases involve complicating factors or assumptions (such as temperatures for comparison). In order to test more conclusively the truth of the consequences of this hypothesis as outlined above, three types of systems were studied experimentally.

In the first the specific conductivities of mixtures of esters and acids were measured. As acids, were chosen acetic, a typical weak acid, and trichloroacetic, a typical strong acid. The conductivities were determined for systems of each of these with ethyl acetate, ethyl benzoate, and benzyl benzoate, these forming a series of esters of increasing acidic strength due to the phenyl group.

The systems of the second type consisted of the ketones, acetone and acetophenone (the first distinctly basic, the second less so) with each of the above acids.

The third type of system had acetic acid as one component together with another acid or a base as the second. Starting with propionic (of about the same strength as acetic) the acid strength of the variable component was increased through monochloroacetic (a transition acid) to the strong acid, trichloroacetic.

Since the conductivities of several systems of bases with acetic acid are recorded in the literature, only one of this type was studied experimentally—that of acetic with formamide. This, together with the systems in the literature, provides material for a series similar to the preceding one, a base being here the variable instead of an acid.

For most of these systems the existence and extent of compound formation have been determined experimentally.² To the others the generalization of Kendall, that stable addition compounds result only from divergence in acidic (or basic) nature of the two components, may be applied with assurance.³

These systems will allow of a thorough test of the correctness of the above discussion of the factors on which the conductivity of a solution depends by furnishing consistent data for quantitative comparisons.

1. *Trans. Far. Soc.*, 6, 71 (1910).

2. Kendall & Booge, *J. A. C. S.*, 38, 1712-36 (1916); Kendall, *J. A. C. S.*, 36, 1722-34 (1914); Kendall & Giggons, *J. A. C. S.*, 37, 149-162 (1915).

3. Lewis—*System of Physical Chem.*, 2d Edition, Vol. I, p. 417.

EXPERIMENTAL

Conductivity Measurements

Since the conductivities were in some cases of the order of pure water (0.5×10^{-7} at 25°), in order to get good sound minima, cells of the type described by Beans and Eastlack¹ with constants from 0.007 to 0.009 were used. The cells were carefully platinized and their constants redetermined frequently during the course of the work. As was found by Beans and Eastlack,¹ no appreciable heating effects were noticed for the solution used.

Capacity effects did not, within the accuracy attained (see later), affect the sharpness of the sound minima. The resistances were measured with a Kohlrausch bridge and telephone receiver (tuned to 1,000 cycles) using current at 1,000 cycles from a constant speed high frequency generator.

Temperatures

The measurements at 25° were made in a thermostat regulates at $25 \pm 0.01^\circ$. At 40° and 60° the bath was constant to 0.05° .

MATERIALS

Great care was exercised in purifying these so as to eliminate very minute amounts of impurities which, though they do not affect the freezing or boiling points except when these constants are measured with extreme accuracy, do nevertheless, affect the conductivity.³

The method of purification was in general as follows: The purest obtainable commercial material was suitably dried (when feasible), then carefully fractionated. For this purpose still-heads of Pyrex glass of an improved design⁴ were used in which the corks were so protected that the hot vapors did not reach them. This effectively prevented any contamination of the product. The thermometers used were carefully standardized and the necessary corrections applied in each case. Boiling points were corrected for pressure in the usual way. Freezing points were determined on from 5 to 10 gms. in an open tube, except in the case of hygroscopic substances which were sealed in small bulbs. Freezing points determined by the usual capillary tube method were found to be worthless for the purpose in hand. The purification and constants of the individual substances are

1. J. A. C. S., 37, 2674 (1915).

2. Loc. cit.

3. See, for example, Walden, Z. physik. Chem., 46, 121 (1903); Schlesinger & Martin, J. A. C. S., 36, 1592 (1914); Davis, Putnam & Jones, J. Franklin Institute, 180, 577 (1915).

4. The operating characteristics of this still, together with details for construction, protection of corks, use in vacuum distillations will be described in a later communication.

given, together with the data, under the head of the various systems.

Measurements of the specific conductivities of mixtures were made approximately every seven molecular per cent. except in the case of systems of very low conductivity. Here only sufficient points (usually six or ten) were determined to conclusively define the position of the curve. In the case of systems with high molecular percentages of trichloroacetic and monochloroacetic acids, the conductivities from about 75 to 100 per cent. of the acid were determined at 60°, this being necessary because of the high M.P. of these acids—59.4° and 63.1°, respectively. (The 100 per cent. monochloroacetic point was easily obtained by supercooling to 60°.) The temperature coefficient was determined on the 75 per cent. mixture (or the nearest point liquid at 25°) and the values at 25°, as plotted in the curves, from 75 to 100 per cent., calculated with the aid of this coefficient. This involves the assumption that the temperature coefficient is independent of the composition and so these portions of the curve are more uncertain than the remainder. The accuracy of the percentage values is in all cases of the order of 0.1 per cent., the mixtures being made by direct weighing. The accuracy of the conductivities is in general not as good as this and varies with the particular system, being about 0.2-0.5 per cent. for systems of the esters with acids, and acids with acids, and from 0.5 to 1 per cent. for acids with ketones and acids with bases. In particular cases, *i. e.*, systems with acetone and formamide, the accuracy is even lower than 1 per cent., due to the extreme difficulty of purifying adequately, and keeping the purified product unchanged. The problem here presents the same aspects as does the preparation of "ultra" conductivity water. Even the largest of the errors which may enter here, cannot, however, affect the validity of the results when considered as evidence for the hypothesis outlined above, since only the *relative magnitudes* of the conductivities of the systems are compared and the differences between these in all cases far exceed the experimental error.

System Trichloroacetic-Ethyl Acetate

Trichloroacetic acid (C.P) was precipitated as fine crystals by rapid cooling from its solution in hot benzene. The crystals were repeatedly washed with cold benzene, the washings being drained off. The residual crystals wet with the benzene were then dissolved by heating and the solution poured hot into a crystallizing dish over 99 per cent. H_2SO_4 in a vacuum desiccator. On cooling the solution deposited crystals and the benzene was taken up in an anhydrous atmosphere by the sulphuric acid, being sulphonated. Very pure trichloroacetic acid of M.P. 59.4° was thus obtained, this being the highest value yet reported.¹ The best conductivity (the samples varied slightly) was 6.2×10^{-9} at 60°. Whetham² gives a resistance of greater than 1×10^7

1. See Kendall & Booge, J. A. C. S., 38, 1723 (1916).

2. Phil. Mag. (5), 44, 1 (1897).

or conductivity less than 1×10^{-7} at 60° for acid melting at 52° . This is obviously only an approximation made with inaccurate apparatus on impure acid.

Ethyl acetate was purified by careful fractionation according to the recommendations of Wade¹ and boiled at 77.1 ± 0.05 . The conductivity was not measureable, being less than 1×10^{-9} . Kahlenberg and Lincoln² found for ethyl acetate distilled over anhydrous copper sulphate 4×10^{-7} . Sammis³ says that ethyl acetate shows no conductivity but gives no limiting value for the measurement.

The data for the system are given in Table I and Fig. I A. Specific conductivities are given in reciprocal ohms $\times 10^{-7}$ and are for 25° , except as noted.

System Acetic-Ethyl Acetate

Acetic acid was first partially purified by successive partial crystallization of the C.P. glacial acid. To carry this through to the pure acid is an exceedingly laborious⁴ and wasteful process, due possibly to the reported formation of mixed crystals.⁵ The freezing point of the partially purified acid was carefully determined and from it the water content calculated, using the figures of De Visser.⁶ The theoretical quantity of redistilled acetic anhydride was then added and the hydrolysis hastened by refluxing at the boiling point for 30 hours, taking care to exclude moisture.

The acid was then carefully fractionated to eliminate salts, etc. (which freezing does not necessarily do), and the large fraction boiling constant at $117.8^\circ \pm 0.17$ used. This froze at $16.57^\circ \pm 0.05$.

The conductivity of the best sample of this acid was $S_{25} = 2.4 \times 10^{-8}$. This is at least as good as the best value in the literature (obtained by Patten⁸ of $< 2 \times 10^{-8}$) and probably better since Patten was using cells with much larger constants and a short bridge and so must have been near the lower limit of his measureable range. The only mention made of this method of obtaining 100 per cent. acetic acid is by Johnstone,⁹ who tried adding the anhydride but evidently did not complete the hydrolysis by heating as he found a higher conductivity after the addition. He attributed this to traces of hydrochloric acid in the anhydride, though more probably it was due to uncombined

1. Wade, J. C. S., 87, 1656-7 (1905).

2. Jour. Phys. Chem., 3, 12-35 (1899).

3. Jour. Phys. Chem., 10, 593-625 (1906).

4. Bousefield & Lowry, J. C. S., 99, 1432 (1911); De Visser Rec. Trav. Chim. Belg., 12, 101 (1893).

5. Ballo, Z. physik. Chem., 72, 439 (1910).

6. Loc. cit., p. 118.

7. See Bousfield & Lowry, Loc. cit., 1432. Also De Visser, Loc. cit., p. 39.

8. Jour. Phys. Chem., 6, 654 (1902).

9. Trans. Nova Scotia Inst. Science, 13, 199 (1913-14).

water and anhydride, both¹ of which, in the light of the present work, would raise the conductivity of the acid.

The data for the system are given in Table II and Fig. II A.

System Ethyl Benzoate-Trichloroacetic

Ethyl benzoate was fractionated under ordinary pressure. The fraction boiling constant at $212.9^\circ \pm 0.1^\circ$ was used and showed a conductivity of $< 1 \times 10^{-9}$. The values for the system are given in Table III and Fig. I B.

System Ethyl Benzoate-Acetic

The values are given in Table IV and Fig. II B.

System Benzyl Benzoate-Trichloroacetic

A search of the literature failed to reveal any reliable constants for benzyl benzoate. Attempts at distillation under ordinary pressure, as recommended by Berkeley,³ resulted in slight cracking and so were abandoned. An improved apparatus for fractionation in vacuum at constant pressure was devised⁴ and the benzyl benzoate fractionated. Since the values of dt/dp which are of the order of 1° per mm. at 10 mm. had to be determined on impure material they would have been inaccurate and would have led to errors in the boiling temperatures and so made comparisons and combination of fractions by boiling points a doubtful procedure. The melting point of each fraction was therefore determined and the fractionation carried out in the usual manner (using these values) until the best fraction gave on redistillation fractions with identical melting points. The melting point of this was $19.3 \pm 0.02^\circ$ and it had a conductivity of $< 1 \times 10^{-9}$. The values in the literature for the melting point vary from $18.3 \pm 0.1^\circ$ to $21 \pm 1.0^\circ$. The higher values are all based on that of Claisen⁵ and were done without exception on small amounts of material with unstandardized thermometers. As pointed out before, especially in the case of a viscous liquid such as benzyl benzoate, the capillary tube method may, unless done with extreme care, lead to wholly incorrect results. The lower value is that of Kendall & Booge⁶ and was determined in an open tube on a large amount of material which, though not so pure, gives a M. P. checking that given here, more closely and in the right direction.

The data for this system are given in Table V, Fig. 2 C.

System Benzyl Benzoate-Acetic

The conductivities for this system with the exception of 100 per cent. acetic were all below 1×10^{-9} and so not measurable. The percentages tried are given in Table VI.

1. Walden, Z. physik. Chem., 54, 161 (1906), finds a high conductivity— 0.383×10^{-6} at 25° for acetic anhydride.

2. Timmerman's Bul. Soc. Chim. de Belg., 25, 300-327 (1911).

3. Berkeley, J. C. S., 109, 520 (1916).

4. To be described later.

5. Ber. 20, 647 (1887).

6. J. A. C. S., 38, 1725 (1916). Compare also Kendall & Monroe, J. A. C. S., 39, 1796 (1917), who give a M. P. 18.8° .

System Trichloroacetic-Acetone

The difficulties incident to the purification of acetone have been noted by various workers.¹ Impurities other than water (and those which form bisulphite compounds) can be gotten rid of by forming the bisulphite addition compound and then hydrolyzing. This, however, still avoids the real difficulty, the elimination of water. The method proposed by Shipsey and Werner,² depending on the formation of a sodium iodide complex, stable at ordinary temperatures, was tried, but, though it gave acetone of correct boiling point, still did not give a low conductivity, due either to the presence of dissolved salt or of water. The method finally resorted to was that recommended by Timmermans³ who, after an exhaustive study of the action of some ten or twelve dehydrating agents on acetone, concluded that the only one which would completely remove the water was phosphorous pentoxide. This, however, has the disadvantage that a loss of about 25 per cent. results from the reaction of the pentoxide with the acetone itself. By cooling in ice water and allowing the solution to stand for several hours, pouring off the acetone and distilling from a small amount of fresh pentoxide, acetone of low conductivity was obtained. This was then carefully fractionated with exclusion of moisture. The boiling point (taken to 0.01°) was here worthless as a criterion, since fractions with the same B.P. would exhibit different conductivities; the fractionation therefore was made by measuring conductivities. In this way, acetone for which $S_{25} = 6 \times 10^{-8}$ was obtained, the best previous value being that of Walden,⁴ $S_{25} = 15 \times 10^{-8}$. Difficulty was experienced in reproducing some of the individual points in the mixture with trichloroacetic, the deviations in some cases amounting to 5 per cent. This was probably due to the varying extent to which the isomeric keto-enol change had proceeded in the presence of differing concentrations of acid and at different times of making measurements. This uncertainty, however, does not affect the relative magnitude of the values as compared with the other systems.

The data are given in Table VII and Fig. III A.

System Acetic-Acetone

The same remarks as made for the preceding system apply here, though the errors were in general smaller. The data are given in Table VIII and Fig. III B.

System Acetophenone-Trichloroacetic

Acetophenone dehydrated with phosphorous pentoxide was fractionated under ordinary pressure and the fraction boiling point constant at $202.3 \pm 0.1^\circ$ used. Care was taken to pour off the acetophenone from the pentoxide before distilling so as to avoid

1. Walden, *Z. physik. Chem.*, **46**, 124 (1903). Timmermans *Bull. Soc. Chim. Belig.*, **24**, 244-6 (1910).
2. J. C. S., **103**, 1255 (1913).
3. Loc. cit.
4. *Z. Physik. Chem.*, **73**, 263 (1910).

the possible formation of benzoic acid during the distillation.¹ The best sample had a value of $S_{25} = 5.5 \times 10^{-8}$. It is possible that this value may be further reduced as one or two very small fractions with still lower values were obtained. Lincoln² found $S_{25} = 18 \times 10^{-8}$. Some of the conductivities are slightly uncertain because, due to shortage of material, it was necessary to use samples of conductivity $C_{25} = 8 \times 10^{-8}$. This is, however, true only of the points near 0 per cent., and 100 per cent. and not for the middle values. The data are given in Table IX and Fig. IV A.

System Acetophenone-Acetic

The data here are given in Table X and Fig. IV B.

System Acetic-Trichloroacetic

The data for these mixtures are given in Table XI and Fig. V A.

System Acetic-Monochloroacetic

Monochloroacetic acid, after crystallization from benzene, was fractioned under ordinary pressure, a large constant boiling fraction being obtained. This was recrystallized several times from benzene, as described under the purification of trichloroacetic acid. Further distillation of this product, which had M.P. $63.1^\circ \pm 0.05$, did not reduce the conductivity which had the exceptionally high value of $S_{60} = 1 \times 10^{-7}$. No value is given in the literature. Whether this high conductivity is due to the presence of small amounts of dichloroacetic or trichloroacetic which are extremely difficult to separate (due to their close boiling points), or whether it bears some relation to the well-known existence of several modifications is uncertain.

The data are given in Table XII and Fig. V B.

System Acetic-Propionic

Propionic acid was prepared by fractional distillation. The conductivity at 25° was less than 1×10^{-9} . Otten³ gives $S_{25} = 7 \times 10^{-8}$. The data are given in Table XIII and Fig. V C.

System Acetic-Formamide

The purification of formamide is a matter of considerable difficulty owing to the ease with which it hydrolyzes and decomposes if heated much above 100° . The chief difficulty consists in the removal of traces of the decomposition products present after its preparation (by heating ammonium formate). Partial freezing is of no avail⁴ the only method which yields a pure product being careful fractionation in vacuo. In this way Davis and Putnam⁵ obtained small fractions with conductivities from 7 to 15×10^{-6} at 25° , and by further fractionation a small quantity for which $S_{25} = 3 \times 10^{-6}$.

1. Compare Klago and Allendorf, *Ber* 31, 1298 (1898).

2. *Trans. Wisconsin Acad.*, 12, II, 395 (1898-9).

3. *Diss. München* (1887).

4. Braun, *J. A. C. S.*, 40, 793 (1918).

5. *J. Frank. Inst.*, 180, 577 (1915).

By repeated fractionation in vacuo several small fractions approximating the best of Davis and Putnam, with values $S_{25} = 4$ to 5×10^{-6} were obtained. The larger portion of the material used, however, had a value of $S_{25} = 9 \times 10^{-6}$. The values for the mixtures in this system are therefore not so reliable as in most of the other systems.¹ The data are given in Table XIV and Fig. VI.

DATA

In the following tables the specific conductivities are in reciprocal ohms at 25° , unless otherwise noted.

The values given in the tables are in all cases those actually measured. For the curves, however, the values at 60° have been calculated to 25° (as explained on page 14), and these latter appear in the curves.

TABLE I

Ethyl Acetate and Trichloroacetic Acid

Mol. % Trichloroacetic	$S \times 10^7$
0.00	< 0.01
4.93	1.10
9.80	2.59
14.36	4.36
19.55	5.94
23.56	7.32
27.31	8.37
30.07 ..	9.12
33.06	9.62
36.67	9.95
42.05	10.05
48.05	9.67
51.52	9.19
54.34	8.74
57.22	8.11
59.07	7.68
63.16	6.82
72.63	3.93
.....	7.02 (60°)
79.12	4.01 (60°)
86.40	1.91 (60°)
94.66	3.74 (60°)
100.00	1.27 (60°)

S—specific conductivity in reciprocal ohms.

1. Compare, however, Davis & Putnam (Loc. cit.), who state that formamide of $S_{25} = 15 \times 10^{-6}$ is, for conductivity measurements on its solutions, practically as good as that of $S_{25} = 7 \times 10^{-6}$.

TABLE II

Ethyl Acetate and Acetic Acid

Mol. % Acetic	$S \times 10^7$
0.00	< 0.01
23.52	0.05
49.27	0.12
77.87	0.20
100.00	0.24

TABLE III

Trichloroacetic and Ethyl Benzoate

Mol. % Trichloroacetic	$S \times 10^7$
0.00	< 0.01
7.95	1.19
17.93	2.08
26.83	2.91
36.59	4.14
47.66	6.32
51.37	7.28
54.81	7.80
58.88	8.26
68.72	7.91
.....	13.91 (60°)
74.97	12.24 (60°)
84.32	7.57 (60°)
92.57	2.54 (60°)
100.00	0.14 (60°)

TABLE IV

Acetic and Ethyl Benzoate

Mol. % Acetic	$S \times 10^7$
0.00	< 0.01
10.15	0.04
28.78	0.08
44.07	0.16
61.45	0.28
74.69	0.38
84.40	0.43
91.74	0.38
100.00	0.24

TABLE V

Trichloroacetic—Benzyl Benzoate

Mol. % Trichloroacetic	$S \times 10^7$
0.00	< 0.01
6.94	0.12
16.25	0.13
26.05	0.16
37.58	0.23
49.28	0.47
57.01	0.68
59.54	0.73
67.25	0.80
74.72	0.84
.....	2.28 (60°)
81.96	2.17 (60°)
88.96	1.37 (60°)
94.50	0.70 (60°)
100.00	0.06 (60°)

TABLE VI

Acetic—Benzyl Benzoate

Mol. % Acetic	$S \times 10^7$
0.00	< 0.01
22.76	< 0.01
73.81	< 0.01
92.62	< 0.01
100.00	0.26

TABLE VII

Acetone and Trichloroacetic Acid

Mol. % Acid	$S \times 10^7$
0.00	0.58
3.37	88.61
6.76	128.4
10.05	163.0
12.52	198.5
16.28	214.5
19.53	222.9
23.04	224.8
26.02	218.9
28.57	205.1
31.81	183.4
40.04	144.1
77.32	118.0
54.17	95.72
59.74	73.84
65.79	54.39
72.47	33.06
76.60	20.23
.....	36.01 (60°)
92.66	2.57 (60°)
100.00	0.06 (60°)

TABLE VIII
Acetone and Acetic Acid

Mol. % Acetic	S $\times 10^7$
0.00	0.58
12.56	3.02
20.27	3.46
28.65	4.19
39.45	4.42
46.03	4.58
51.04	5.08
64.92	4.80
71.43	4.32
81.10	3.12
92.23	1.33
100.00	0.26

TABLE IX
Trichloroacetic—Acetophenone

Mol. % Trichloroacetic	S $\times 10^7$
0.00	0.9
6.83	11.39
14.04	15.96
24.60	20.10
36.92	21.35
44.15	21.41
48.42	21.66
53.23	22.38
59.94	22.57
66.64	20.84
72.42	16.88
71.37	17.77
.....	44.43 (60°)
79.27	27.94 (60°)
87.38	10.57 (60°)
95.16	1.48 (60°)
100.00	0.06 (60°)

TABLE X
Acetic—Acetophenone

Mol. % Acetic	S $\times 10^7$
0.00	0.9
6.91	2.86
16.39	3.33
25.39	3.51
33.29	3.58
40.98	3.46
49.55	3.44
57.22	3.20
65.87	2.83
69.68	2.59
77.20	2.26
82.79	1.75
90.74	1.11
100.00	0.24

TABLE XI
Acetic—Trichloracetic

Mol. % Acetic	$S \times 10^7$
0.00	0.05 (60°)
9.47	0.38 (60°)
17.63	1.04 (60°)
28.27	2.91 (60°)
.....	0.84 (25°)
31.66	1.15
39.61	2.25
47.61	3.80
55.13	5.64
62.01	7.10
68.25	8.08
72.33	8.31
76.28	8.05
81.28	6.37
89.57	3.67
95.14	1.67
100.00	0.26

TABLE XII
Acetic—Chloracetic

Mol. % Acetic	$S \times 10^7$
0.00	14.11 (60°)
6.80	14.67 (60°)
15.87	15.33 (60°)
25.19	15.64 (60°)
31.79	15.54 (60°)
.....	5.59 (25°)
44.80	5.27
50.40	5.03
59.84	4.55
69.50	3.84
76.98	2.99
85.24	1.92
92.75	0.98
100.00	0.25

TABLE XIII
System Acetic—Propionic

Mol. % Acetic	$S \times 10^7$
0.00	< 0.01
8.86	0.03
25.37	0.06
45.41	0.07
71.20	0.13
92.49	0.18
100.00	0.24

TABLE XIV

System Acetic—Formamide

Mol. % Acetic Acid	$S \times 10^7$
0.00	91.37
4.82	177.2
15.89	515.0
19.99	605.4
26.59	641.8
35.52	629.2
46.85 ¹	515.7
55.26	448.1
63.58	380.3
71.58	300.5
78.95	201.4
88.92	33.88
96.00	4.36
100.00	0.25

DISCUSSION OF RESULTS

The conductivities of the pure liquids used may first be compared. In making such comparison it is to be noted that though some of the actual values are probably too high, it is doubtful that further attempts at purification will lower their order of magnitude materially. This statement is applicable with assurance to the esters, ketones and acids, with the exception of chloracetic acid and possibly acetophenone.² A further disturbing factor which will affect the actual magnitude of the conductivity is the viscosity. In general the viscosity will be greater the larger the normal molecular weight or the more the liquid is associated.³ On the other hand the conductivity decreases with increasing viscosity.⁴ The effect of association will be, therefore, to increase the conductivity as previously discussed. This increase will, however, be counterbalanced to a certain extent by the increased viscosity accompanying the association. In the following table the association factors are from the compilation of Walden.⁵ The chloracetic acids are not included

1. In order to compare the effect of temperature on conductivity with that on viscosity, the conductivity of this mixture (46.85%) was determined at 40° also, and gave $S_{40} \times 10^7$ equals 923.4. The viscosities for the system have been determined at 25° and 40° (Merry & Turner, J. C. S., 105, 758 (1914)).

2. Thus Walden, Z. physik. Chem., 46, 145 (1903), considered Formamide for which $S_{25} = 4.7 \times 10^{-6}$ as pure; also (Z. physik. Chem., 73, 2633 (1910), acetone of $S_{25} = 1.5 \times 10^{-7}$. Even the differences (which are far less likely of recurrence) between these values and those given below do not seriously affect the validity of the comparison.

3. Dunstan & Thole. Viscosity of liquids.

4. See in this connection Walden, Z. physik. Chem., 55, 246 (1906).

5. Z. physik Chem., 39, 561 (1902).

since their conductivities were measured at 60° and the rest of the data are lacking for them:

Substance.	Association Factor.	Table XV.	
		S X 10 ⁷ .	Viscosity at 25°.
Formamide	6.18	3.0	0.03358
Water	3.81	0.55	0.00893
Acetic	3.62	0.24	0.01194
Acetone	1.26	0.58	0.00346
Acetophenone	1.16	0.55	0.0180
Propionic		0.01	0.0102
Ethyl Acetate	1.00	0.01	0.00449
Ethyl Benzoate	1.00	0.01	0.01991
Benzyl Benzoate	1.00	0.01	0.08454

The effects of association and viscosity are well brought out by this table. Thus formamide with an association factor almost twice that of water has a conductivity considerably higher than water in spite of its larger viscosity. On the other hand the low viscosity of acetone more than counteracts the higher association of water and acetic acid. Also acetic acid with an association factor but little different from that of water yet has only half the conductivity, due to its considerably higher viscosity.

The esters being practically non-associated exhibit no conductivity even when they have low viscosities as in the case of ethyl acetate.

A more strictly quantitative discussion of the conductivity of pure liquids is impossible because of the uncertainty as to the correct values for the association factors. The evidence here presented, however (combined with that given in the Table on p. 3), clearly substantiates the statements made regarding the connection between the ionization of a pure liquid and its association. In order to discuss more exactly the effect of viscosity on the conductivities of these particular liquids and their mixtures, an accurate examination of their viscosities is at present being undertaken.

SOLUTIONS

In the system ethyl acetate—acetic, since the two components are not very different in character, no compound formation will take place, and consequently the ionization and conductivity will be practically the same as that of the two components. We find this to be the case (Fig. II A). Trichloroacetic acid and ethyl acetate which are of widely different character form a compound (M.P.—27°)¹. Due to this decided divergence in character (and the fact² that the measurement is made considerably (52°) above its M.P), the compound should be ionically unstable and give a comparatively good conducting solution. In point of fact the maximum conductivity for the system (Fig. I A) is about 140 times that of its higher valued component. The

1. Kendall & Booge, J. A. C. S., 38, 1723 (1916).

2. The effect of temperature on conductance in binary systems is taken up in a later section.

effect of viscosity is noticed in the shifting of the maximum toward the ethyl acetate, the component of lower viscosity. The comparison of these two systems brings out clearly the effect of increasing diversity.

In the systems of the two acids with ethyl benzoate this is again emphasized. The lower conductivity for the system with trichloroacetic than with ethyl acetate (Fig. I) is accounted for by (1) the more similar acidic nature, (2) the more stable compounds (M.P.—23°)¹ and (3) the higher viscosity (Table 15), the latter resulting in moving the maximum point away from the more viscous ethyl benzoate.

On the other hand the system ethyl benzoate with acetic (Fig. II B), while exhibiting a slight maximum, is nevertheless far below that with trichloroacetic. Comparison of the acetic—ethyl acetate and acetic-ethyl benzoate curves shows (Fig. II) higher values for the conductivity of the latter. This is the opposite of what at first sight might be expected from analogy with the curves (Fig. I) of these two esters with trichloroacetic acid where the positions are reversed. The cause of this difference is very likely a "common ion" effect. That is one ion present in pure acetic (from the ionization of the associated acetic molecules) is probably the same as one ion resulting from the ionization of whatever small amount of an acetic—ethyl acetate complex there may be present, thus causing a mutual repression and less ionization.

For the system, benzyl benzoate—Trichloroacetic, following upon (1) the smaller divergence in character of the components, and (2) the existence of a compound whose ionic stability (only 13° above its M.P. (11.90°) will be greater than that of the compounds in the preceding systems, there should result a poorly conducting solution. The high viscosity of the benzyl benzoate here shifts the maximum toward the high trichloroacetic concentration (Fig. II C). The conductivities, while lower than for the previous system with trichloroacetic, are still well above those for the acetic systems.

Benzyl benzoate with acetic acid, owing to the absence of compound formation and the high viscosity, gives, as was to be expected, a system with conductivities below 1×10^{-9} for all values measured (Table VI).

In considering the systems of the ketones with the two acids, the decided basic nature of the ketone is of importance. There should be manifest here more *extensive* compound formation than in the case of the esters. Thus acetone (of low melting point) can be expected to form complexes of several types with the strong acid, trichloroacetic. Owing to their complexity and the fact that the measurements were made at 25° (a temperature which must be considerably above their melting points) the compounds would be ionically unstable and so give good conducting solutions. Further the very low viscosity of acetone should enable the conductivity to reach considerable values in the solutions containing high percentages of acetone. Reference

1. Kendall & Booge, Loc. cit., p. 1724.

to Fig. III A show that this is the case. The maximum has a value over 350 times that of the pure components and is shifted far toward the acetone side.

Even with acetone and the *weak acid*, acetic, these factors (*i. e.*, basicity of acetone and low melting points and viscosities) make the conductivities of the system comparable with those of the less basic esters with the *strong acid*, trichloroacetic. (Compare Tables I, III, VIII and Figs. I and III). The smaller difference in the viscosities and melting points of the components accounts for the greater symmetry of the curve.

In the systems with acetophenone, the influence of the acidic phenyl group becomes evident in the lower conductivities relative to the acetone systems. Thus with trichloroacetic, acetophenone forms a single equimolecular compound of M.P. 26° . The flatness of the freezing point curve¹ indicates considerable dissociation, however. The effect of these influences is reflected in the conductivity curve (Fig. IV A). There the symmetry is more marked, due to the closer viscosities and melting points, than in the case of acetone. The stability of the compound at its maximum and the increased viscosity resulting from its supercooling (from 26° to 25°) appear in the sharp change of direction between 40 and 60 per cent., which amounts almost to a minimum. Even here, however, the actual values of the conductivities are still fairly high when compared with the ester systems.

The lower values in the system acetophenone—acetic follow from the smaller divergence between the two components, though they are still higher than for the corresponding ester systems (Figs. II and IV B).

Turning to the systems of acetic with acids, we find that as the difference between the acidic strength of the variable component and that of the acetic increases, better conducting systems are obtained. Thus trichloroacetic forms with acetic compounds, stable only in the liquid.² It will therefore give a conducting system (Fig. V A), though the order of conductivity will be comparatively low, both components being acidic. Again with the weaker acid, monochloroacetic, no stable compound is formed, though the slight difference in acidic strength induces combination in the liquid to a certain extent. A flat maximum in the conductivity curve is to be expected, and this is exactly what is obtained (Fig. V B).

For the acids acetic and propionic, the mixtures should, owing to the closeness of the acidic strengths, have conductivities but little different from those of the two components. The curve (Fig. V C) is, in fact, practically linear.

Comparisons of the systems of bases with acetic acid are unfortunately likely to be unreliable, due to our lack of knowledge of their true constants as bases. This arises from their amphoteric nature. Thus water, as well as being a weak acid and base, is also a salt. Similarly the amines and amides form inner salts.

1. See Kendall & Gibbons, J. A. C. S., 37, p. 153 (1915).

2. See Kendall, J. A. C. S., 36, 1733 (1914).

Predictions as to *comparative* conductivities in some of these systems are therefore uncertain due to the difficulty in distinguishing the conductivity due to the base from that due to the inner salt. In general the same regulations are evident in systems of bases with acetic as in those of acids and acetic previously considered. This is seen in a series of amines. Patten¹ has measured the conductivities of systems of acetic acid with aniline, dimethylaniline, isobutyl amine, and amyl amine at 25°. The last two aliphatic amines, with constants as bases in aqueous solution of $K_{25} = 10^{-4}$, form quite stable one-one compounds with the acetic. This is shown by a minimum conductivity in each case at 50 molecular per cent. These are instances where one of the possible types of compounds is fairly stable with respect to the ionic dissociation as well as to the dissociation into the original components. A more poorly defined example of this was seen in the system acetophenone—acetic. The good conduction in these systems probably results from the ionic disintegration of higher order complexes, which should be present, due to the diversity of the original components.

The two aromatic amines have (due to the phenyl group) less basic properties ($K_{25} = 10^{-10}$). The conductivities of their mixtures with acetic acid are lower than for the aliphatic amines and exhibit no minima.

Further comparison of these amines among themselves (*i. e.*, of amyl with isobutyl amine or aniline with dimethyl aniline) is not warranted since their constants are probably only correct as to the order of magnitude.

In like manner the system acetic—water² shows smaller conductivities than does the system acetic—aniline. This is what is to be expected from the weaker basic properties of the water ($K_{\text{base}} = 2 \times 10^{-16}$) relative to the aniline ($K_{\text{base}} = 1 \times 10^{-10}$) making the difference between the acetic and water less than that between the acetic and aniline.

It is unfortunate that no figures are available for the basic strength of formamide so that the system acetic—formamide might be included in the above series, as numerous other data are also available for it. The presence of a compound consisting of two molecules of acetic to one of formamide ($2\text{CH}_3\text{COOH} \cdot \text{HCONH}_2$)—barely stable at its maximum, has been shown by English and Turner.³ The form of the curves indicates the presence of other compounds of different order. The viscosities⁴ of the system also exhibit a maximum at about 60 per cent. formamide at 25°. The conductivities (Fig. VI) show a maximum at about 75 per cent. formamide and then fall rather sharply, the curve becoming slightly concave. The maximum occurs where the stability of the complexes (as shown by the freezing points) is low. With increasing acetic concentration the conductivities decrease as the comparatively stable two-

1. J. Physik Chem., 6, 580 (1902).

2. Kohlrausch & Holborn, "Leitvermögen der Elektrolyten."

3. English & Turner, J. C. S., 107, 777 (1915).

4. Merry & Turner, J. C. S., 105, 758 (1914).

one compound is formed with its higher viscosity and lower conductivity.

Effect of Temperature

The influence of temperature on conductivity has been alluded to several times but a more careful analysis of the way in which conductivity varies with temperature seems desirable.

Three factors have important bearing on this variation:

(a) The association of the original components of the solution (or that of a pure liquid) decreases with rise of temperature.

(b) With rise of temperature the complexes become unstable, both with respect to the ionic dissociation and to that into the original components. The complexes of different order will also in general have different stabilities.

(c) The velocity of the ions will increase at higher temperatures in consequence of the diminished viscosity and complexity.

These three factors will, as a rule, all be present in a given case, the balance between them determining the actual value of the conductivity rather than any one of them alone. Thus in the system acetic-formamide¹ the temperature coefficient for decrease in viscosity² is smaller than that for the increase of conductivity in the same interval. The first two factors must, therefore, also be considered. The balance between these effects and the varying importance of each at different temperatures is illustrated in the well-known case of water, whose temperature conductivity curve exhibits at maximum between 200° and 300°. Other illustrations of these factors have already been pointed out in the discussion of the individual systems.

CONCLUSION

It will be seen from the preceding discussion of the individual systems that the results are in general in excellent agreement with theoretical basis which was developed in the beginning of the paper and, therefore, furnish evidence as to the probable correctness of the hypothesis there advanced.

1. See Note to Table XIV.

2. Merry & Turner, *J. C. S.*, 105, 758 (1914).

SUMMARY

In an attempt to extend and generalize the current ionization theory so as to cover finite concentrations and deal with non-aqueous solution:

(1) The hypothesis has been advanced that ionization in solution is preceded by compound formation between solvent and solute, and the factors determining the presence and extent of such solvent-solute complexes being known.

(2) The ionization of these complexes is postulated as the cause of conductivity in solutions (and in the special case, of pure liquids).

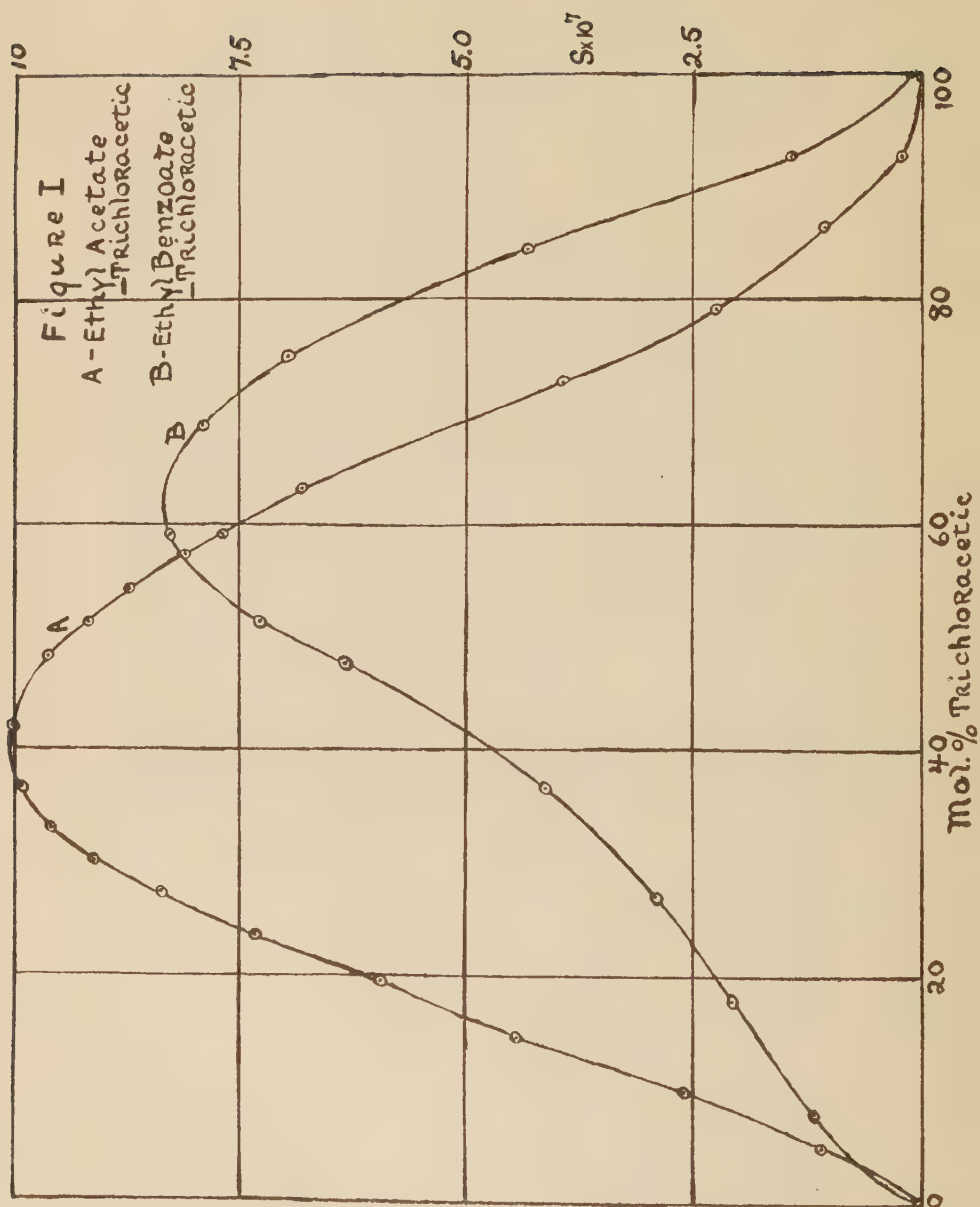
(3) The factors affecting the ionic dissociation of complexes have been formulated and discussed with the aid of illustrations from the literature.

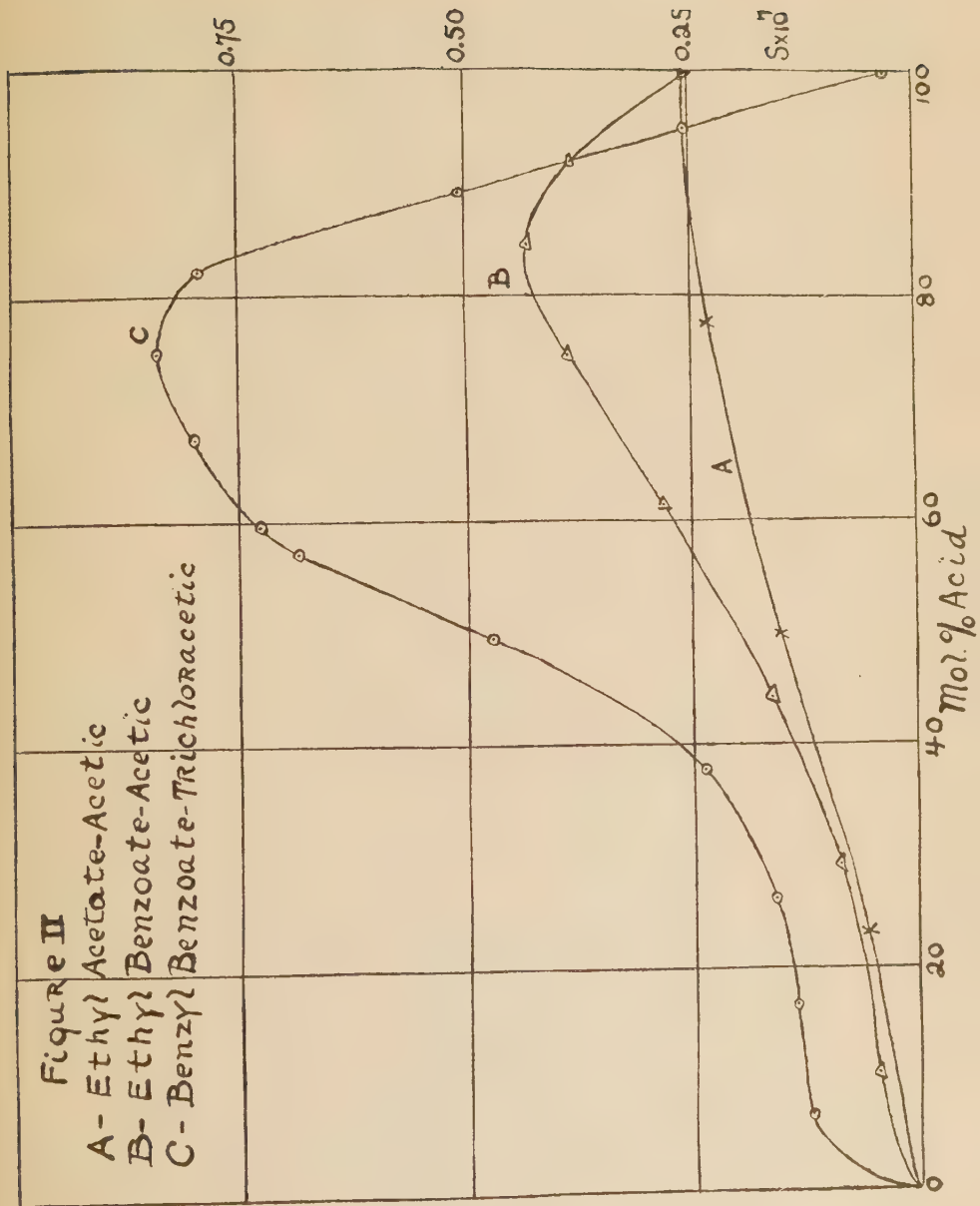
(4) In order to more thoroughly test the conclusions arrived at, the specific conductivities of fourteen systems of the general type acid -X (where X is an ester, ketone, acid or base) were determined, both the components being varied through a wide range.

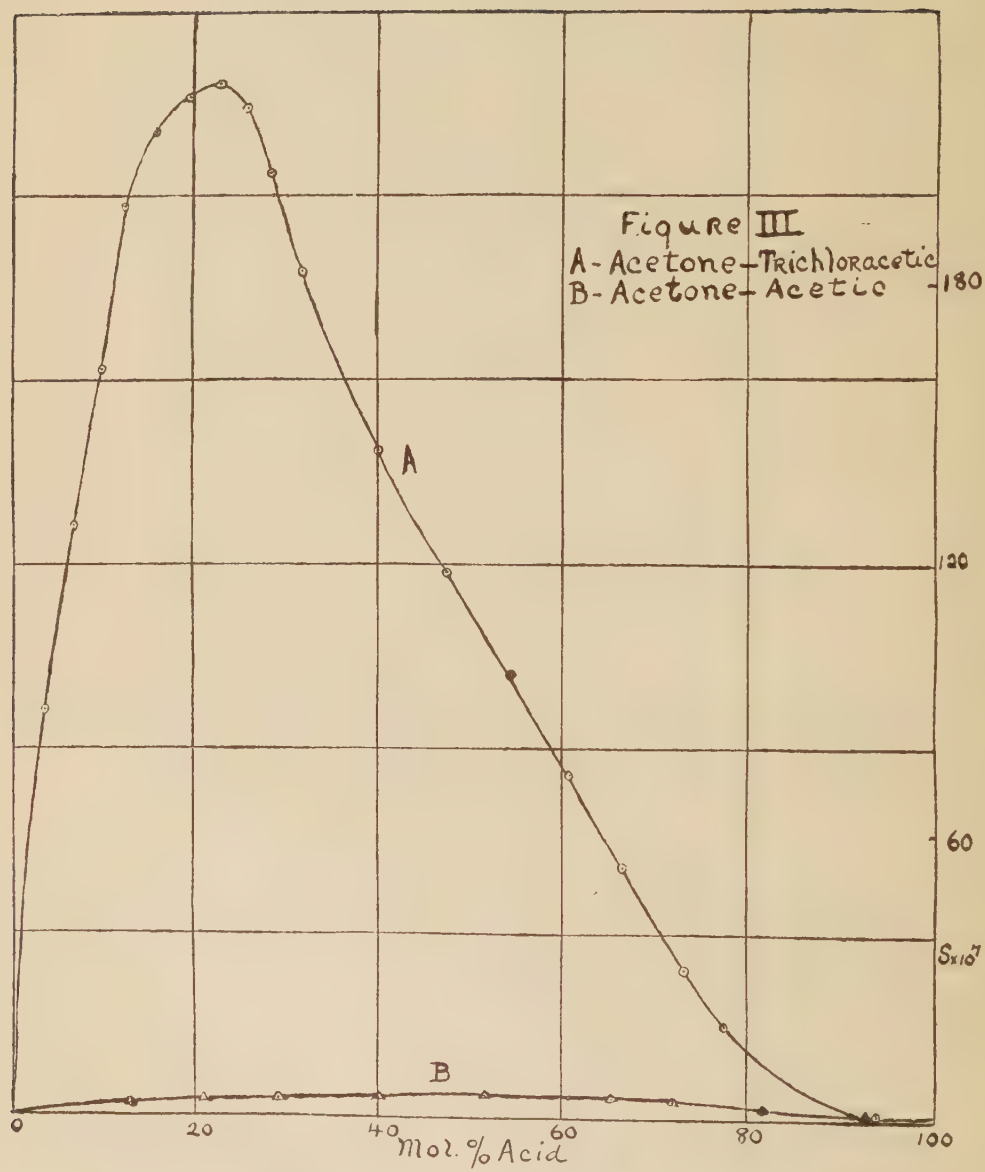
(4) A discussion of the results has shown them to be strong evidence confirmatory of the correctness of the hypothesis and the deductions therefrom.

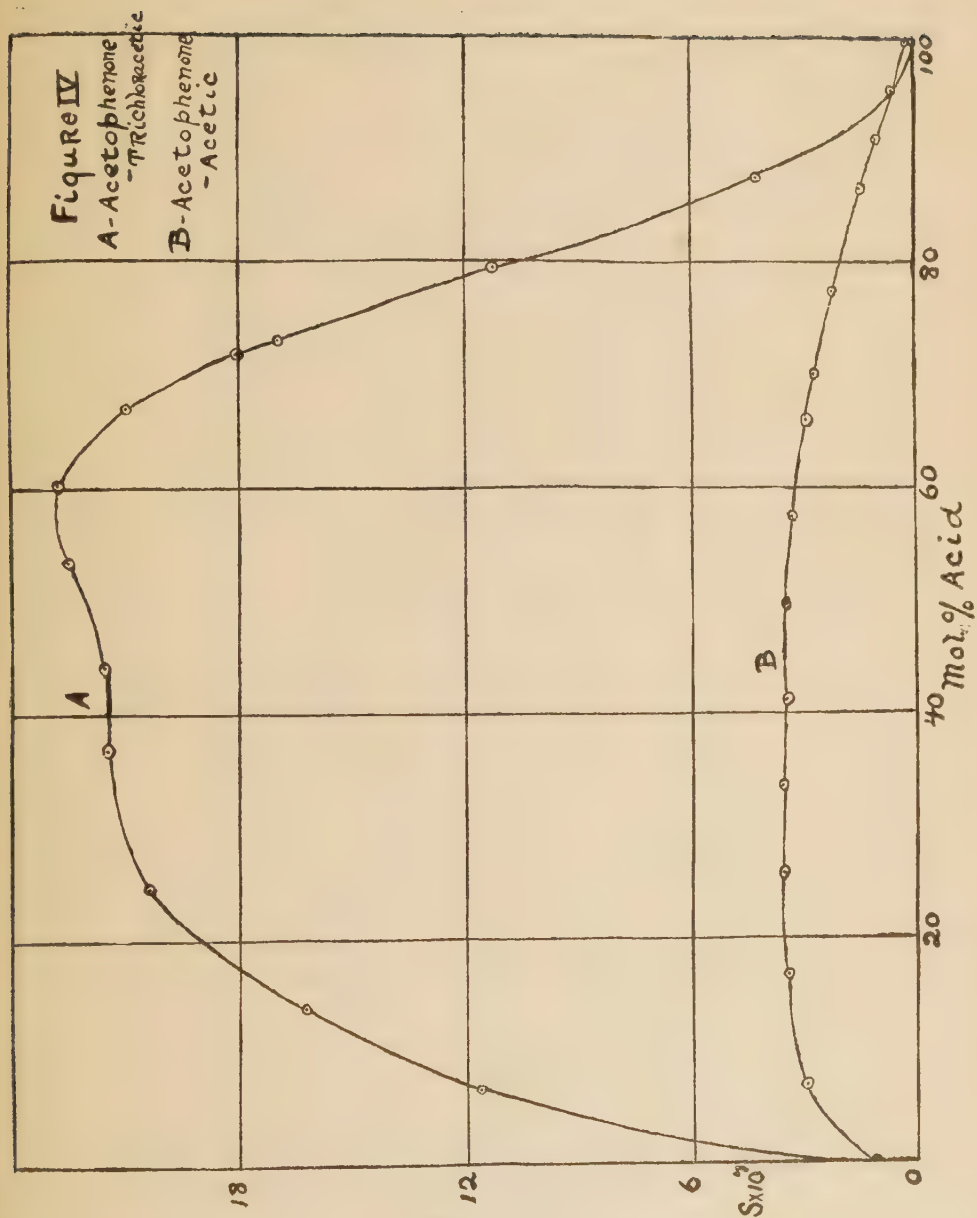
VITA

Paul Magnus Gross was born in New York City on September 15, 1895, and attended the grade and high schools of that city. He received the degree of B.S. from the College of the City of New York in February, 1916. From 1916 to 1918 he taught in the Department of Chemistry of the College of the City of New York. He entered the graduate school of Columbia University in February, 1916, and in February, 1917, received from Columbia the degree of M.A. in chemistry. In 1918 he discontinued his teaching and graduate work to enter the Chemical Warfare Service of the United States Army as 2d Lieutenant. In January, 1919, he resumed graduate work at Columbia University, and held an Instructorship in the Summer Session of the University. He is co-author of a paper entitled, *A Study of the Methods for the Quantitative Determination of Aluminum in Blood*, printed in the Biochemical Bulletin, Volume V, Nos. 20-21, April-May, 1916.









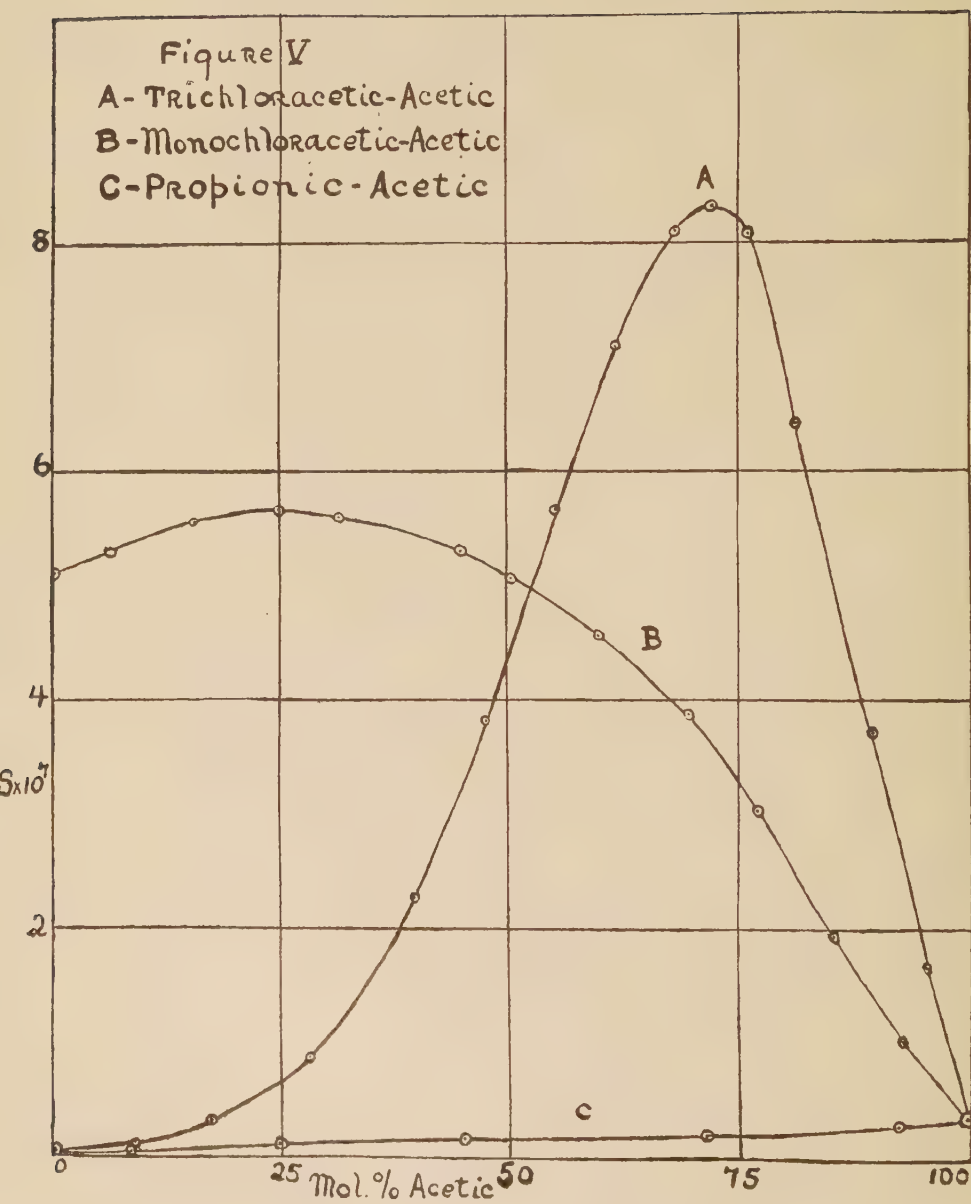


FIGURE VI
Formamide-Acetic

